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Ambient Air Monitoring After an Application of Oxydemeton-Methyl in Monterey County During September 1995

Engineering and Laboratory Branch
Monitoring and Laboratory Division

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APPROVED:

Don Fitzell, Project Engineer

Cynthia L. Castronovo, Manager,
Testing Section

George Lew, Chief,
Engineering and Laboratory Branch

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This report presents the results of ambient air monitoring after a ground application by tractor of oxydemeton-methyl (Metasystox R, MSR) at a selected cauliflower field in Monterey County. Samples were collected before, during and for 72 hours after the start of the application. No samples analyzed contained oxydemeton-methyl or its primary breakdown product, dioxydemeton-methyl, above the limit of quantitation, 0.25 ug/sample (0.097 ug/m^3 for a three hour sample at a flowrate of 14.4 lpm.) Eighteen out of the forty (excluding the blank) collected field samples contained trace levels (between 0.05 and 0.25 ug/sample) of one or the other compound.

Acknowledgments

Jack LaBrue of the Air Resources Board was the Instrument Technician. George Hurley and Toby Price of Western Farm Service arranged for a suitable field to monitor. Assistance was also provided by Cara Roderick and Ruth Tomlin of the ARB's Air Quality Measures Branch.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

APPENDICES

Ambient Air Monitoring After an Application of Oxydemeton-methyl
in Monterey County During September 1995

I. INTRODUCTION

The Air Resources Board's (ARB) Engineering and Laboratory Branch (ELB) staff conducted a three-day source impacted ambient monitoring program after an application of oxydemeton-methyl (Metasystox R, MSR) to a cauliflower field in Monterey County during September of 1995. The samples were analyzed for oxydemeton-methyl and its primary breakdown product, dioxydemeton-methyl. This monitoring was performed at the request of the California Department of Pesticide Regulation (DPR). This monitoring occurred from September 12 through September 15, 1995. As required by Food and Agricultural Code Section 14021, this monitoring was conducted to provide DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

As part of the requirement of DPR, the ARB also conducted ambient monitoring of oxydemeton-methyl in Monterey County around the same time as the application monitoring reported here. The results of the ambient monitoring are presented in the ARB report, "Ambient Air Monitoring for Oxydemeton-methyl in Monterey County During August and September 1995."

The Pesticide Use Report for 1994 indicates oxydemeton-methyl is most widely used on broccoli (52,282 pounds), cauliflower (23,627 pounds), sugar beets (9,288 pounds) and cabbage (8,729 pounds).

This monitoring was a follow-up to similar sampling conducted in September 1992 which found no measurable levels of oxydemeton-methyl or dioxydemeton-methyl in either ambient or application monitoring. The present monitoring was undertaken because it was felt the limits of quantitation for a 24-hour sample (6.0 ug/m^3 for oxydemeton-methyl and 4.5 ug/m^3 for dioxydemeton-methyl) in the previous study were not low enough to evaluate the potential health risks.

II. DESCRIPTION

Oxydemeton-methyl (molecular weight 246.29 g/mole) is a colorless liquid with a vapor pressure of 3.83×10^{-5} mm Hg at 25°C. It is only slightly soluble in water (approx. 1.0×10^{5} ppm), but is readily soluble in dichloromethane, 2-propanol and toluene.

Oxydemeton-methyl is regulated as a restricted use material under Section 6400, Title 3 of the California Code of Regulations and classified a Category I pesticide by the United States Environmental Protection Agency (US EPA). Peak use of this insecticide occurs in Monterey County during late summer (July, August and September).

The acute oral and dermal LD_{50} (rat) for oxydemeton-methyl is 60 mg/kg and 112 mg/kg,

respectively. Female rat and mouse LC_{50} values are 1.5 and 0.51 mg/L, respectively. (DPR's Monitoring Recommendation, APPENDIX I.)

III. SAMPLING LOCATIONS

A cauliflower field of about 14 acres (FIGURE I) was selected by George Hurley of Western Farm Service and approved by ARB staff for application monitoring. Four sites were used (see FIGURE II): one on the northwestern perimeter (site NW) at a distance of about 15 yards from the field and about 20 feet above the field, one about 5 yards from the eastern corner (site E) at a height of about 5 feet, one (a collocated site with 2 samplers) about 5 yards from the southeastern side (site SE) at a height of about 6 feet and one approximately 7 yards from the southwestern side of the field (site SW) at a height of about 5 feet. A meteorological station with a strip chart recorder was set up near site SE to determine wind speed and direction. A second meteorological station equipped with a data logger was also set up. Site SE took duplicate samples to determine precision of the data. All other sites collected single samples.

The application was by two tractors and took just under an hour. The application began in the northern corner. The tractors traversed from north to south and from northwest to southwest. Metasystox-R (25% active ingredient) was applied at a rate of 1 quart per acre. Also applied were: Lorsban 50WSP (active ingredient 50% chlorpyrifos) at 1.5 pound per acre, Asana XL (active ingredient 8.4% Esfenvalerate) an insecticide at 7.0 ounces per acre, Buffercide (phosphoric acid) at 1.0 pint per acre and Nu-film-P, a sticker-spreader at 0.25 pint per acre. The application was made at night. The work order for this application is in APPENDIX II.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through a Teflon holder containing approximately 30 cc of XAD-4 resin (see APPENDIX III). The resin was held in place by installing stainless steel screens on each side of the resin and between the Teflon support rings. Any oxydemeton-methyl or its breakdown product present in the sampled ambient air was captured by the XAD-4 adsorbent. Subsequent to sampling, the resin was transferred into a glass jar with a Teflon-lined lid and stored in an ice chest containing dry ice. All samples were transported on dry ice to the Trace Analytical Laboratory (TAL) of the Department of Environmental Toxicology, University of California, Davis for analysis.

Each sample train consisted of an XAD-4 resin holder, Teflon fittings and tubing, control valve, rotometer, train support, and a 12VDC powered vacuum pump. A diagram of the sampling train is shown in APPENDIX III, Attachment I. Aluminum foil was wrapped around the holder to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through the holders adjusted with a metering valve to an indicated reading of 15.0 liters per minute (lpm) on the rotometer. A leak check was performed by blocking off the sample inlet. The sampling train would be considered to

be leak free if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 15.0 lpm. The starting flowrate (if different from the 15.0 lpm) along with date, time and site location were recorded in the field log book. Calibration prior to use in the field indicated that an average flow rate of 14.4 lpm was actually achieved when the flow meter was set to 15.0. At the end of each sampling period the final indicated flow rate (if different than the set 15.0), the stop date and time were recorded. If the final flow rate changed from the original 15.0 lpm, the average of the initial and the final flow rates was used to calculate the total volume of sampled air. The sampling schedule outlined in the QA Plan for Pesticide Monitoring APPENDIX II, Attachment II) was modified to avoid a "midnight run" to change the sampling tubes.

V. ANALYTICAL METHODOLOGY

The XAD-4 resin recovered from each sampler was analyzed by the TAL staff. The XAD-4 resin was extracted with 75 ml ethyl acetate. An aliquot of the extract was evaporated to dryness then redissolved in acetone prior to analysis using gas chromatography/nitrogen-phosphorus detector (GC/NPD). This analysis was to determine levels of the breakdown product, dioxydemeton-methyl, present in the sample.

A second aliquot was oxidized and analyzed for combined dioxydemeton-methyl (any originally in the sample plus any oxydemeton-methyl present which would be oxidized to the breakdown product, dioxydemeton-methyl) using GC/NPD. The level of oxydemeton-methyl was calculated by subtracting the non-oxidized results from the oxidized results from the same sample. A detailed description of the method is presented in the TAL Report (APPENDIX IV).

VI. RESULTS

The monitoring results are shown in TABLE I. A summary of the on-site meteorological data is presented in TABLE II. Additional detailed meteorological data from the California Irrigation Management Information System (CIMIS) station, located north of Salinas, is presented in APPENDIX V. None of the results presented in this report have been corrected for percentage recovery.

No samples analyzed contained oxydemeton-methyl or its primary breakdown product, dioxydemeton-methyl, above the limit of quantitation, 0.25 ug/sample (0.097 ug/m^3 for a three hour sample at a flowrate of 14.4 lpm) for each compound. Eighteen out of the forty (excluding the blank) collected field samples contained trace levels (between 0.05 and 0.25 ug/sample) of one or the other compound. In this report, if the TAL was unable to quantify the level, it is reported as not detected (ND). The TAL Report (APPENDIX IV) identifies the samples which contained trace levels.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the TAL Report, (APPENDIX IV).

Most of the procedures outlined in the Quality Assurance Plan for Pesticide Monitoring (APPENDIX III, Attachment II) were followed. The only exception was a modification of the sampling schedule (see SAMPLING METHODOLOGY). In addition, a flow rate audit, a systems audit and an analytical performance audit were performed by the Quality Management and Operations Support Branch (QMOSB) (see APPENDIX VI).

The TAL staff prepared field spikes which accurately represented the handling in the field. The field spike results ranged from 109% to 121% for oxydemeton-methyl and 120% to 140% for dioxydemeton-methyl.

Laboratory spikes were prepared by the TAL as well as the ARB's QMOSB. Recovery for the ARB audit spikes averaged 89% and 114% for oxydemeton-methyl and its breakdown product, respectively. The TAL in-house application spike recovery levels averaged 95% and 129% for these compounds. The complete results of the TAL spikes and QMOSB audit are presented in APPENDIX IV and APPENDIX VI, respectively.

FIGURE I. Oxydemeton Methyl Monitoring Area

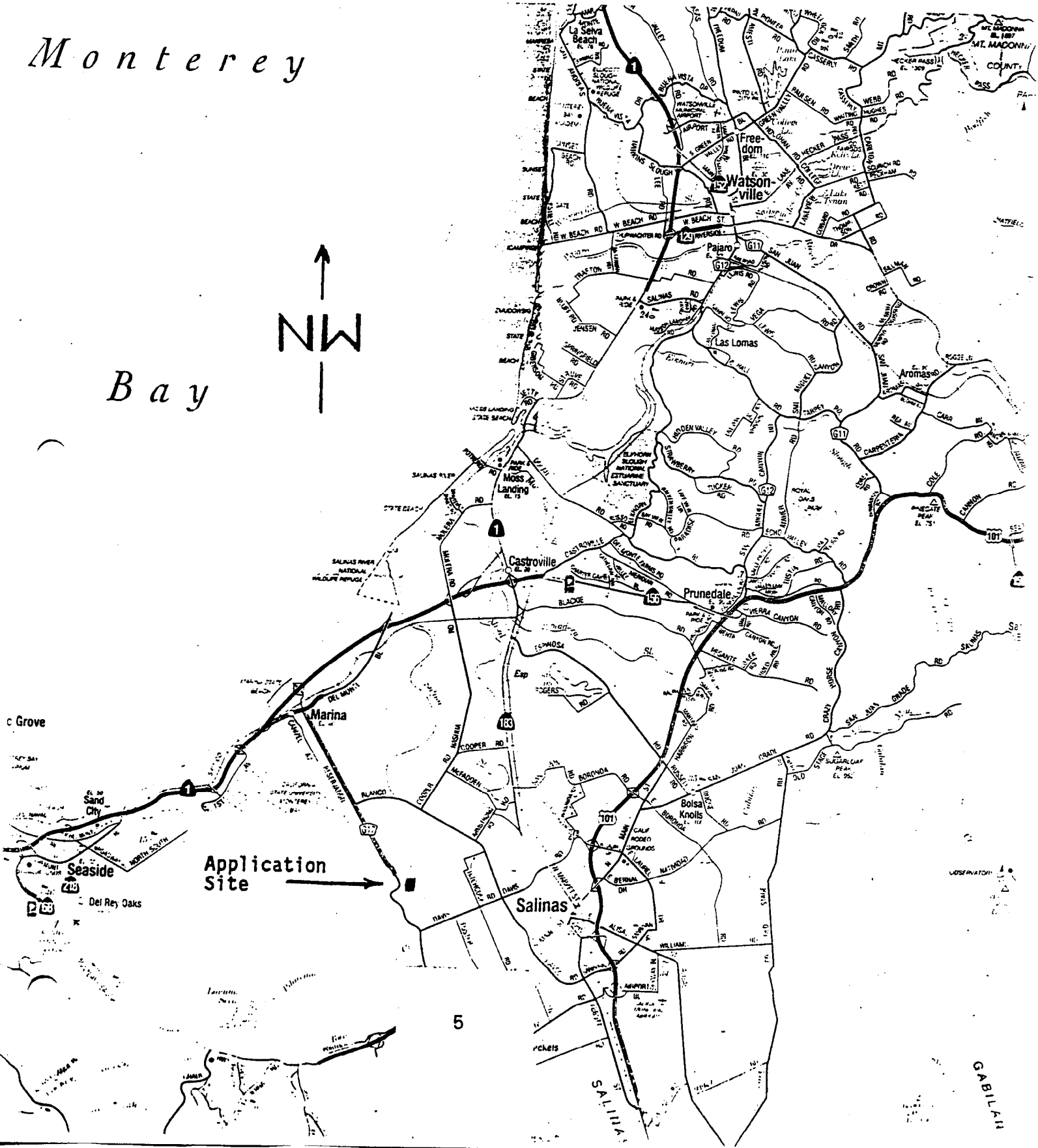
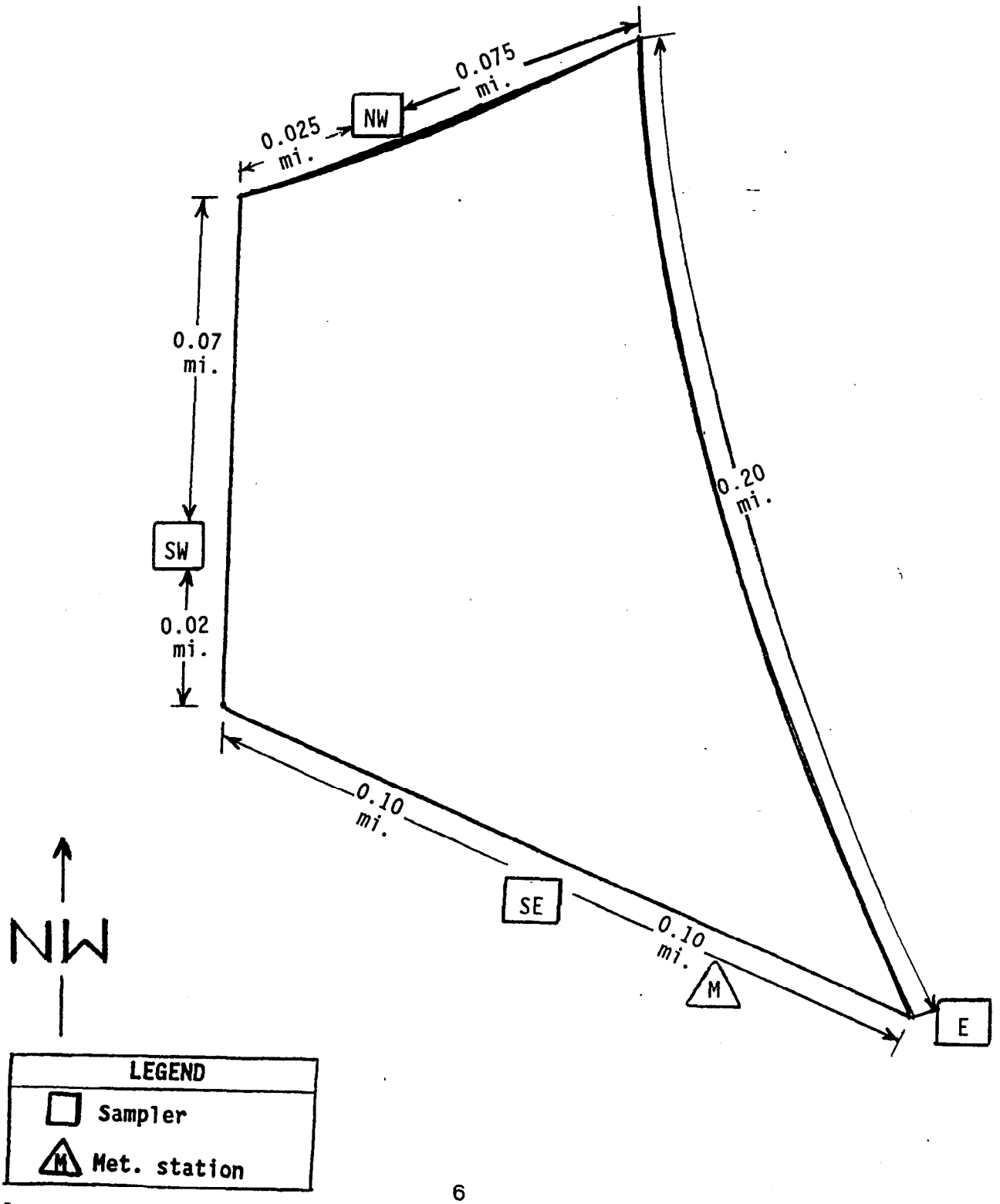


FIGURE II. Oxydemeton Methyl Monitoring Sites



All measurements are approximate.

TABLE I. Oxydemeton-methyl Application Monitoring Data

Sample ID	Time (min.)	Volume (m^3)	Total (ug)	Concentration (ug/m^3)	Collection Time (Approx.)
0NW	595	8.57	ND	--	
0E	605	8.71	ND	--	Background
0SE-1	610	8.78	ND	--	
0SE-2	610	8.78	ND	--	9/11-12/95
0SW	625	9.00	ND	--	(1730-0400)
1NW	160	2.30	ND	--	
1E	165	2.38	ND	--	(Application)
1SE-1	170	2.45	ND	--	
1SE-2	170	2.45	ND	--	9/12/95
1SW	175	2.52	ND	--	(0400-0700)
2NW	165	2.38	ND	--	
2E	170	2.45	ND	--	
2SE-1	170	2.45	ND	--	
2SE-2	170	2.45	ND	--	
2SW	170	2.45	ND	--	9/12/95
2B	BLANK	--	ND	--	(0700-1000)
3NW	245	3.53	ND	--	
3E	250	3.60	ND	--	
3SE-1	250	3.60	ND	--	
3SE-2	250	3.60	ND	--	9/12/95
3SW	255	3.67	ND	--	(1000-1400)

[1]All flows at 14.4 liters per minute unless otherwise noted. (see SAMPLING METHODOLOGY).

*Flowrate decreased during the run. The average of the starting and ending flowrate was used to calculate the volume sampled.

ND = Not Detected, <0.25 ug/sample.

No values corrected for percentage of recovery.

TABLE I. Oxydemeton-methyl Application Monitoring Data (cont.)

Sample ID	Time (min.)	Volume (m^3)	Total (ug)	Concentration (ug/m^3)	Collection Time (Approx.)
4NW	310	4.46	ND	--	
4E	300	4.32	ND	--	
4SE-1	300	4.32	ND	--	
4SE-2	300	4.32	ND	--	9/12/95
4SW	295	4.25	ND	--	(1400-1900)
5NW	720	10.4	ND	--	
5E	Sample lost				
5SE-1	730	10.5	ND	--	
5SE-2	730	10.5	ND	--	9/12-13/95
5SW	735	10.6	ND	--	(1900-0730)
6NW*	1440	20.4	ND	--	
6E*	1435	19.0	ND	--	
6SE-1	1435	20.7	ND	--	
6SE-2	1435	20.7	ND	--	9/13-14/95
6SW	1435	20.7	ND	--	(0730-0730)
7NW	1380	19.9	ND	--	
7E*	1435	18.4	ND	--	
7SE-1	1430	20.6	ND	--	
7SE-2	1430	20.6	ND	--	9/14-15/95
7SW	1430	20.6	ND	--	(0730-0700)

[1]All flows at 14.4 liters per minute (see SAMPLING METHODOLOGY).

*Flowrate decreased during the run. The average of the starting and ending flowrate was used to calculate the volume sampled.

ND = Not Detected, <0.25 ug/sample.
No values corrected for percentage of recovery.

TABLE II. Oxydemeton-methyl Meteorological Data

Sampling Period	Wind Direction	Wind Speed (mph)	Cloud Cover
0	**WNW**/SW/W/NW	5	PC/O
1	SE/E/S	3	PC/O
2	SE/E/S/NW	3	PC/O
3	**NW**/N/NE	4	PC/O
4	**NW**/W	9	PC/O
5	**W**/NW/SW/S	5	PC/O
6	**W**/**NW**/N/SW	6	PC/O
7	**SW**/**W**/NW	7	PC/O

BOLD indicates predominant wind direction, if any.

Indicates direction wind blows from.

K = clear, PC = partly cloudy, O = overcast